

## Phonon Assisted Tunnel Ionization of Deep Impurities in the Electric Field of Far-Infrared Radiation

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Ionization of semiconductor deep impurity centers has been observed in the far infrared, where photon energies are several factors of 10 smaller than the binding energy of the impurities. It is shown that the ionization is caused by phonon assisted tunneling in the electric field of the high power radiation. This optical method allows the investigation of the tunneling process at electric bias fields well below the threshold of avalanche breakdown.

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We report on the first observation of the photoionization of deep impurity levels in a semiconductor by a radiation field with photon energies much less than the ionization energy of impurities. The photoconductivity of gold and mercury doped germanium has been observed and investigated using a high power pulsed far-infrared (FIR) laser source. A photoconductive signal, rising exponentially with the incident power, could be detected in spite of the fact that the photon energy of the exciting radiation is several factors of 10 less than the binding energy of the impurities,  $E_i$ . The experimental results give strong evidence that the ionization of deep impurity centers by radiation with photon energy  $\hbar\omega \ll E_i$  is caused by tunnel ionization in the strong optical field. It has been previously shown that the thermal emission of deeply bound electrons becomes possible in an electric field due to a phonon assisted tunnel effect even if  $k_B T < E_i$  [1]. The electric field produces an almost triangular energy barrier and electron tunneling through that barrier yield a total ionization probability of  $W(E) = W_0 \exp(F/F_c)^2$ , where  $F$  is the force acting on the electron in the electric field and  $F_c$  is the characteristic force [2]. Tunnel ionization has been extensively studied in semiconductors subjected to static electric fields [1–6]. In the present paper we show that the same process may occur in an optical field of frequency  $\omega < \omega_v$ , where  $\omega_v$  is the local vibration frequency at the impurity site.

The measurements were carried out on *p*-type germanium with gold and mercury impurities having ionization energies of  $E_i \sim 150$  meV and 90 meV, respectively [1]. The deep acceptor density was in the range of  $10^{14}$  cm $^{-3}$  to  $10^{15}$  cm $^{-3}$ . The radiation source used was a pulsed FIR molecular laser optically pumped by a TEA CO $_2$  laser. Using NH $_3$  and D $_2$ O as active gases, 40 ns pulses with a peak power of 50 kW were obtained at wavelengths,  $\lambda$ , of 90.5  $\mu$ m, 152  $\mu$ m, and 250  $\mu$ m. The corresponding photon energies of 13.7 meV, 8.2 meV, and 5 meV are much smaller than the ionization energies of the impurities.

The Ge samples were placed in a temperature vari-

able optical cryostat. Measurements have been carried out in the temperature range between 20 K and 77 K where practically all charge carriers are frozen in to the impurity ground states. The FIR absorption was unmeasurably small therefore heating of the sample may be neglected. A series of cold and warm black polyethylene (1 mm thick), Teflon, and crystal quartz windows were used to transmit far-infrared radiation while rejecting near-infrared and visible light. The photoconductive signal was measured using a standard 50  $\Omega$  load resistor circuit, taking care that the bias voltage at the sample was substantially below the threshold of electric breakdown. A photoconductive response was found at all three wavelengths. The decay time of the observed signal was about 50 ns for Ge(Hg) and 80 ns for Ge(Au), i.e., somewhat longer than the laser pulse but much shorter than that of a thermal source, e.g., by heating of windows. Thus the decay time represents the lifetime of the excited impurity levels [7,8]. The sign of the photoconductive signal corresponds to a decrease in sample resistance and thus to an increase in the free carrier concentration. These observations demonstrate that the photoionization of deep impurities by light with  $\hbar\omega \ll E_i$  takes place. In Fig. 1 the photoconductive signal of Ge doped with gold ( $E_i \sim 150$  meV) at  $T = 77$  K is shown as a function of radiation intensity for  $\lambda = 90.5$   $\mu$ m. The signal is a strongly nonlinear function of intensity  $I$ , following approximately the relation  $V \propto \exp(I/I_c) - 1$ , where  $I_c$  is a characteristic intensity. The same dependence has been observed for germanium doped with mercury but the photoionization takes place here at a lower level of irradiation intensity.

The photoionization of deep impurities by light with  $\hbar\omega \ll E_i$  and the strong nonlinear dependence of this process on intensity may be associated with three mechanisms of nonequilibrium carrier creation, namely, multiphoton absorption, light impact ionization, and tunnel ionization in the optical field. Two-photon transitions [9] and, more recently, light impact ionization of impurities [10] have been observed in the far infrared. Multiphoton ionization of atomlike centers has been theoretically

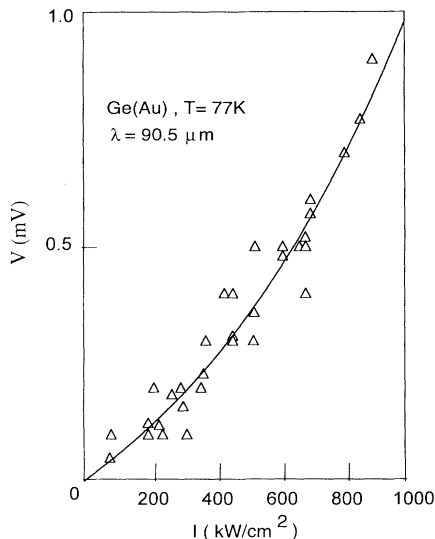


FIG. 1. Photoconductivity signal of Au doped *p*-Ge (binding energy  $E_i \sim 150$  meV) as a function of intensity at  $\lambda = 90.5 \mu\text{m}$  (photon energy 13.7 meV) and  $T = 77$  K. The bias voltage was 5 V. The full line is a fit by  $V = V_0[\exp(I/I_c) - 1]$ .

treated by Keldysh [11] but to our knowledge there are no experimental investigations of impurity multiphoton ionization in semiconductors. Both processes show a distinct dependence on irradiation frequency. Increasing the excitation frequency raises the generation rate of nonequilibrium electrons as a result of multiphoton absorption whereas the rate decreases in the case of light impact ionization. In contrast, tunnel ionization in the field of an optical wave is expected to be independent of the frequency as long as the radiation frequency is substantially smaller than the vibration frequency of the impurity. In order to ensure reliable identification of the photoexcitation mechanism, we carried out additional power dependence measurements at wavelengths of  $152 \mu\text{m}$  and  $250 \mu\text{m}$ . These experiments have shown that an increase in the radiation wavelength does not change the relation between excess carrier generation and irradiation intensity. The signal for a given irradiation intensity does not depend on the wavelength in the present spectral range. In Fig. 2 the relative photoconductive signal  $(\Delta\sigma/\sigma)$  is shown in a log-linear plot as function of the square of the amplitude of the radiation field for both impurities and all three wavelengths. Within the accuracy of the measurement, the curves for different wavelengths coincide. This allows us to rule out multiphoton absorption as well as light impact ionization and unambiguously indicates that the deep impurity ionization is here due to tunnel ionization in the optical field. Such processes have been experimentally and theoretically investigated in detail for the case of a static electric field [1-6].

If the energy of phonons is less than impurity binding energy, deep impurities may be thermally ionized by

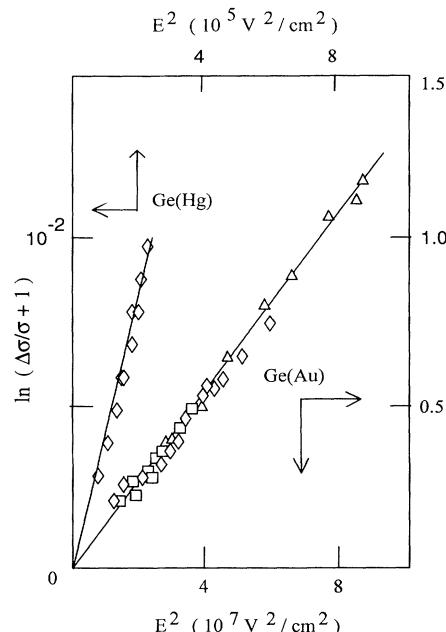


FIG. 2. The dependence of  $\ln(\Delta\sigma/\sigma + 1)$  for Ge(Au), ( $E_i \sim 150$  meV) at 77 K on the square of the amplitude of the optical electric field  $E$  at three wavelengths  $\lambda = 90.5 \mu\text{m}$  (13.7 meV,  $\Delta$ ),  $152 \mu\text{m}$  (8.2 meV,  $\square$ ), and  $250 \mu\text{m}$  (5 meV,  $\diamond$ ). For the purpose of comparison, an analogous measurement on Ge(Hg) ( $E_i \sim 90$  meV) at  $\lambda = 90.5 \mu\text{m}$  (13.7 meV) is also shown. Note the different abscissa and ordinate scales.

the multiphonon processes. The presence of a sufficiently strong electric field increases the emission rate of free carriers by tunneling processes. This mechanism is discussed within the adiabatic approximation. Figure 3 shows the electronic energy in a weak electric field as a function of a configurational coordinate  $x$  [1]. Curves  $U_1$  and  $U_2$  correspond to the bound state of the hole at the center and the ionized center, respectively. The transition of holes from  $U_1$  to  $U_1$  is favored when the elongation of the configurational coordinate is close to the crossing point  $x^*$  of both potential curves. This requires the rather high energy of  $\varepsilon_T + \varepsilon_c$ . Therefore thermoionization proceeds usually via tunneling of the impurity from curve  $U_1$  to curve  $U_2$  at a vibration energy only slightly exceeding the thermal binding energy  $\varepsilon_T$  [1,2]. In the presence of an electric field the hole tunneling enhances this process because the final state is now reduced in energy. This is shown in Fig. 3 by the potential curve  $U_e$  located below the term  $U_2$ . The higher the electric field strength, the greater the decrease of the term  $U_e$  with a corresponding increase in hole tunnel rate and ionization probability. Because the radiation frequency used in our experiments is less than the impurity vibration frequency, this adiabatic model may be applied assuming tunneling in the electric field of the radiation. In the case of weak electric fields [ $E < (2m\varepsilon_T)^{1/2}/\tau_2$ , where  $\tau_2$  is the tunneling time], which corresponds to the present experimental

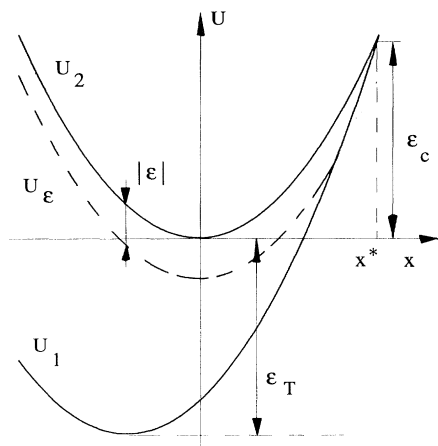


FIG. 3. Schematic representation of the adiabatic electronic potential as a function of a configuration coordinate of impurity motion,  $x$ .  $\epsilon_T$  is the thermal binding energy. Solid curves  $U_1$  and  $U_2$  correspond to the hole bound to the center and detached from the impurity at the bottom of the valence band ( $\epsilon = 0$ ), respectively. The dashed curve  $U_\epsilon$  is the potential of the ionized impurity in a weak electric field.

conditions, the total probability of ionization depends on the electric field [2] as

$$W_i = W_0 \exp(E^2/E_c^2), \quad (1)$$

where  $E_c^2 = 3m\hbar^2/\tau_2^3$  and

$$\tau_2 = \hbar/2kT + \tau_1. \quad (2)$$

$W_0$  is the thermal emission probability without electric field,  $E_c$  is the characteristic field intensity, and  $\hbar/2\tau_1$  is of the order of the phonon energy. Equation (1) is valid for neutral impurity centers. In fact, gold and mercury are charged centers in germanium. This leads to an additional multiplicative term in the ionization probability [1]. In the present range of electric field strengths, however, this correction is close to unity and thus may be omitted.

Figure 2 shows the experimentally determined dependence of  $\ln(\Delta\sigma/\sigma + 1)$  on the square of the amplitude of the optical electric field for three different wavelengths. Because the duration of the light pulses is shorter than the capture time of nonequilibrium carriers, recombination may be ignored during the excitation. Therefore the experimentally determined relative change in photoconductivity,  $\Delta\sigma/\sigma$ , of  $p$ -Ge is equal to  $\Delta p/p$  where  $p$  is the free carrier concentration. Measurements at  $T = 77$  K are plotted for  $p$ -Ge(Au) and  $p$ -Ge(Hg) with impurity concentrations of  $7 \times 10^{14} \text{ cm}^{-3}$  and  $4 \times 10^{14} \text{ cm}^{-3}$ , respectively. It is seen that the probability of photoexcitation depends on the electric field as  $\exp(E^2/E_c^2) - 1$ . The magnitude of the characteristic field  $E_c$  does not depend on the wavelength but it is significantly lower for lower temperatures. These results are in good agreement with

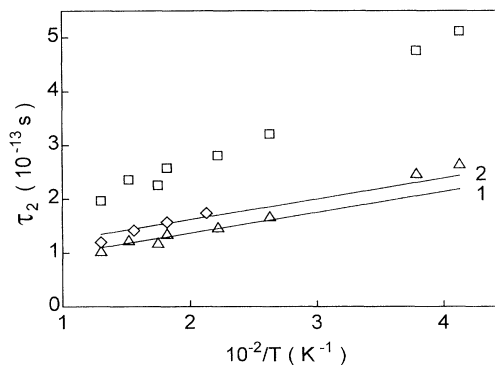


FIG. 4. Tunneling time  $\tau_2$  calculated from the experimental characteristic fields as function of inverse temperature. Triangles and squares: Ge(Au) using light and heavy hole masses, respectively. Diamonds: Ge(Hg) using light hole mass. Curve 1 and curve 2 show calculations after  $\tau_2 = \tau_1 + \hbar/2kT$  with  $\tau_1$  equal to  $6 \times 10^{-14}$  s and  $8 \times 10^{-14}$  s, respectively.

Eq. (1). As is seen from this relation, tunneling times  $\tau_2$  can be derived from the values of the characteristic field. In order to calculate them it is necessary to know what kind of mass is responsible for tunneling. In Fig. 4 the tunneling time  $\tau_2$  as function of the inverse temperature is shown for both impurities. Using the light hole mass for evaluation excellent quantitative agreement to Eq. (2) is found. This allows us to conclude that tunneling is accomplished predominantly by light holes.

In summary, we have observed for the first time the photoionization of deep impurity centers in a semiconductor by far-infrared radiation with quantum energies much smaller than the impurity ionization energy. This is attributed to ionization by phonon assisted tunneling in the field of the high power radiation. The effect of an electric field on the thermal emission and capture of carriers is of great importance for the kinetics and dynamics of semiconductors. Ionizing deep impurities in high static electric fields usually drives the system into avalanche breakdown. This substantially changes the properties of the semiconductor and disguises the elementary process of tunneling. The present method of ionizing deep impurities in the far-infrared optical fields allows the study of phonon assisted tunnel processes in a range of static electric field strengths well below the threshold breakdown, i.e., where the perturbation of the electron system is small. This is accomplished utilizing the intrinsically high sensitivity of photoconductivity which yields a measurable signal from a few photoexcited carriers.

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